CXXII.—The Effect of Temperature and of Pressure on the Equilibrium $2CO \equiv CO_2 + C$.

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IN extension of van't Hoff's principle of mobile equilibrium to include all the factors that determine chemical equilibrium in gaseous systems, Le Chatelier's theorem states that any change in the factors of equilibrium from outside is followed by a reverse change within the system.

At constant temperature and pressure the reaction

$2CO \longrightarrow CO_2 + C$

is accompanied by a decrease in volume. A decrease in pressure should, therefore, increase the proportion of carbon monoxide in the system $2CO \rightleftharpoons CO_2 + C$ in equilibrium at constant temperature.

The general formula deduced by Le Chatelier:

$$500 \int L \frac{dT}{T} + (N' - N) \log_e P + \log_e \frac{C_1^{n_1} \cdot C'_1^{n_1} \cdot \cdots}{C_2^{n_2} \cdot C'_2^{n_2} \cdot \cdots} = k,$$

which, when P was assumed constant and equal to one atmosphere, we have shown to hold for changes in temperature (Trans., 1910, **97**, 2178), contains the expression $(N'-N)\log_{e} P$, by means of which changes in pressure should be accounted for.

When P=1, this expression disappears from the formula, and on introducing the known values for the system under consideration, the equation becomes:

$$\frac{19,500}{T} + \log_e \frac{C_1^2}{C_2} = k.$$

In our previous communication we have given values for k for different temperatures, calculated from this equation, the method of experiment being such as to leave the gases under as nearly as possible atmospheric pressure when equilibrium had been reached.

We are not acquainted with any previous attempts to prove whether the expression $(N'-N)\log_e P$ in Le Chatelier's general equation satisfies experiment in this particular case, and since the matter is one of considerable importance in several allied investigations, we have undertaken its determination.

Since for the system $2CO \implies CO_2 + C$, N' = 2 and N = 1, the effect on k of pressure should be measured directly by the natural logarithm of the value of the latter in atmospheres, and the determination of k for different pressures at any one temperature should be sufficient to verify the equation.

AND OF PRESSURE ON THE EQUILIBRIUM $2CO \equiv CO_2 + C$ 1141

Our former values for k at different temperatures showed, however, a tendency towards an increase as the equilibrium temperature was increased. We were therefore desirous of ascertaining whether this is actually the case, or whether the alterations in the value of the constant should be ascribed solely to experimental error. For this purpose we have made a considerable number of determinations of the percentages of carbon dioxide and monoxide remaining in equilibrium over carbon at different temperatures and pressures, reaching the equilibrium from both directions.

Our method of experiment, which is described in detail later, is very similar to that employed by Boudouard (Ann. Chim. Phys., 1901, [vii], **24**, 5), the chief difference being that whereas Boudouard's determinations were all made at constant pressure (atmospheric), ours have been chiefly at constant volume, the pressure produced by the expansion of the gases on raising them to the experimental temperature, and (when starting with an initial concentration of 100 per cent. carbon dioxide) by the formation of two volumes of carbon monoxide for each volume of carbon dioxide changed, enabling us to study the effect of a fairly high pressure on the equilibrium values.

The values obtained for the equilibrium constant at any one temperature for different pressures agree remarkably well, as the following determinations at 1273° Abs. (the temperature at which the majority of our experiments have been made) show:

Experiment No. P 10. Temperature=1273° Abs.

Pressures, atmospheres.	C_1 .	C_2 .	k.
3.08	0.9723	0.0277	19.98
2.43	0.9776	0.0224	19 96
2.02	0.9837	0.0163	20.11
1.56	0.9856	0.0144	19 98
0.66	0.9935	0.0062	20.14

We are therefore justified in introducing values for $\log_e P$ in the equation:

$$\frac{19,500}{T} + \log_e P + \log_e \frac{C_1^2}{C_2} = k . \qquad . \qquad . \qquad (i)$$

to correct for divergencies from 760 mm. pressure in our previous series of determinations.

At the same time we may remark that an error of 10° in either direction in the measurement of temperature alters the value of the constant by a quantity decreasing from 0.16 at 1123° Abs. to 0.09 at 1473° Abs. Errors in analysis of the gases have a greater effect on the constant at high than at low temperatures; that is to

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say, the effect of error is greater when the percentage of carbon dioxide present is small. If, for example, 6.25 per cent. of carbon dioxide were remaining in equilibrium at 1123°, instead of the 6.23 per cent. recorded, the numerical value of the constant alters only in the third decimal place; whilst at 1473° a similar error of 0.02 per cent. in the determination of carbon dioxide alters the value of the constant from 20.65 to 20.36.

We give below our previous values for k at different temperatures corrected for pressure, and also the corrections to be applied for an error of 10° in the temperature measurements and of 0.02 per cent. in the determination of carbon dioxide.

Temperature. °Abs.	<i>k</i> .	Correction for error of 10° in measurement of temperature.	Correction for error of 0 02 per cent. in estimation of carbon dioxide.
1123	20.00	+ 0.16	\mathbf{nil}
1173	20.29	0.15	nil
1223	20.23	0.14	+0.05
1273	20.36	0.12	- _{0.03}
1323	20.30	0.11	0.04
1373	20 58	0.10	0.14
1473	20.60	0.09	0.29

It will thus be seen that, if one assumes both errors to lie in the negative direction at the higher, and in the positive direction at the lower temperatures, the apparent increase in the value of the constant at high temperatures loses its significance so long as only a few determinations are relied on; for we cannot pretend to an accuracy of 0.02 per cent. in the estimation of small quantities of carbon dioxide. When, however, as in the present case, a number of closely agreeing values are obtained at each temperature, one is justified in considering either that the experimental error is not so great as surmised, or, what is more probable, that the "personal factor," which exercises its influence particularly on gas analysis, tends to throw the error always in the same direction.

Our results again indicate an increase in the value of the equilibrium constant with increased temperature, as calculated from equation (i). The numbers increase from an average of 19.85 for 1073° Abs. (pressures from 1 to 3 atmospheres) to 20.16 for 1373° Abs. (pressures from 0.5 to 3 atmospheres).

These values, and those for intermediate temperatures given in the table that follows, are lower than those previously given, a result which we must attribute to differences in the experimental method employed. In particular, an unavoidable alteration in the method of measuring the temperatures appears to us most likely to render the results of the two series not strictly comparable. In

AND OF PRESSURE ON THE EQUILIBRIUM $2CO \equiv CO_2 + C$. 1143

the former series a protected thermo-couple was embedded in the carbon, whilst in the present series the thermo-couple had to be placed outside the reaction vessel, and was in immediate contact with the furnace tube. The average temperature of the reacting surface may therefore have been lower than the recorded temperature in the present series, whilst in the former arrangement the carbon near the walls of the porcelain tube was possibly at a higher temperature than that immediately surrounding the thermo-couple.

The mean values at different temperatures of those obtained at all pressures are:

Temperature.	
⁵ Abs.	<i>k</i> .
1073	19.85
1173	19.96
1223	20.01
1273	20.04
1322	20.14
1373	20.17

We do not think that the progressive increase in the value of k, which appears to be a linear increase over the range of temperature studied, should be ignored. We presume it to be due to the decrease with temperature of the value of L (the total heat of the reaction), dependent on the difference of the specific heats of the two systems, for which no allowance is made in Le Chatelier's equation.

Assuming for the moment a linear increase in the value of the constant, which can then be expressed as a function of T and has a value 18.777 + 0.001 T, calculation gives the following quantities of carbon dioxide and carbon monoxide in equilibrium over carbon at atmospheric pressure and at different temperatures:

Temperature.	со.	CO ₂ .	
Abs.	C_1 .	C_2 .	Value of k used.
1073	0.8615	0.1385	19.85
1123	0.9313	0.0687	19.90
1173	0.9663	0.0337	19.95
1223	0.9833	0.0167	20.00
1273	0.9915	0.0085	20.05
1323	0.6822	0.0042	20.10
1373	0.9975	0.0025	20.12

We will now substitute a corrected value for L_r in equation (i), and determine the value of the equilibrium constant on introducing the values for C_1 and C_2 given in the above table.

Taking the heat of reaction at ordinary temperatures and at constant volume to be

 $2CO = CO_2 + C + 38,380$ gram-calories,

we have for the difference between the molecular heats of factors and products *:

$$\begin{array}{c} 2\text{CO} = 8 \cdot 94 + 0 \cdot 0012 \, T \\ \text{CO}_2 = \\ \text{C} = \\ \hline \\ = \\ \hline \\ = 2 \cdot 02 - 0 \cdot 0031 \, T \\ = 2 \cdot 02 - 0 \cdot 0031 \, T \end{array} \\ \begin{array}{c} 5 \cdot 28 + 0 \cdot 0026 \, T \\ \hline 1 \cdot 64 + 0 \cdot 0017 \, T \\ \hline 1 \cdot 64 + 0 \cdot 0017 \, T \\ \hline \\ = 2 \cdot 02 - 0 \cdot 0031 \, T \end{array}$$

from which is obtained the value for L_0 (the heat of reaction at absolute zero) 38,055, so that the value of L_T , obtained from the expression \dagger :

 $L_T = L_0 + \sigma'_v T + \sigma'' T^2$

becomes $38,055 + 2.02T - 0.0031T^2$.

* The expressions used for the molecular heats of carbon dioxide and carbon monoxide are obtained from the formulæ given by Langen (*Dingl. polytech. J.*, 1903, **318**, 433) for the mean thermal capacity of the gases over the range 0 to t° :

For CO $C_v = 4.8 + 0.0006t$

,, $CO_2 \quad C_v = 6.7 + 0.0026t$.

+ According to Kirchoff's law the change in the value of the reaction heat with temperature depends on the difference between the molecular heats of the substances used up (factors) and of the substances formed (products) in the reaction. Adopting Haber's generalisation (*Thermodynamics of Technical Gas Reactions*, 1908, p. 27), if we imagine (1) the reaction to take place at the temperature T with a gain of heat L_r , and the resulting products to be then cooled down to absolute zero, we should obtain the same net amount of heat as though (2) we had first cooled the factors of the reaction to absolute zero and then allowed the reaction to proceed with a gain of heat, L_0 .

If $C_{y(0,T)}$ be the mean molecular heat of the products between 0° and T° , then the net gain of heat according to the first mode of procedure (1) would be $L_T + TC_{y(0,T)}$; and according to the second (2) it would be $L_0 + TC_{x(0,T)}$, where $C_{x(0,T)}$ is the mean molecular heat of the factors. Since these two quantities are equal:

$$L_T = L_0 + T(C_{x(0,T)} - C'_{y(0,T)}).$$

The effect of temperature on the mean molecular heat of each substance can be expressed by the empirical formula:

$$C_v = a + b T + c T^2 + \ldots \dots$$

Only the first two constants, however, a and b, can be determined with any degree of accuracy, so that the mean thermal capacity of each substance taking part in the reaction must be represented by the approximation: $C_v = a + bT$. We can then write for the mean molecular heats of all the factors (all at constant volume):

and for the products :

$$C_{factors} = \Xi a + T \Xi b,$$
$$C_{products} = \Xi a^* + T \Xi b^*.$$

Making use of Kirchoff's law we get for the reaction heat at absolute zero the expression :

$$L_T - L_0 + T(\Xi a - \Xi a^*) + T^2(\Xi b - \Xi b^*).$$

If we call $\Xi \alpha - \Xi \alpha^*$ (the difference between the sum of the *a*'s of the factors and the sum of the *a*'s of the products), σ'_v , and $\Xi b - \Xi b^*$ (the difference between the sum of the *b*'s of the factors and the sum of the *b*'s of the products), σ'' , we get the formula $L_T = L_0 + \sigma'_v T + \sigma'' T^2$ used above. As Haber points out (*loc. cit.*, p. 49), the term σ'' does not need the index *v*, since it has the same value whether molecular heat at constant volume or constant pressure is meant.

AND OF PRESSURE ON THE EQUILIBRIUM $2CO \equiv CO_2 + C$. 1145

In this calculation some uncertainty arises from the formula used for the atomic heat of carbon. It is obtained from the determinations made by Kunz (Ann. Physik, 1904, [iv], **14**, 327) for the mean specific heat of wood charcoal, as follow:

Between 0° and 435°	561°	728°	925°	1059°	1197°	1297°
s = 0.243	0.290	0.328	0.328	0.362	0.378	0.381

which find expression in the formula:

 $s = 0.2143 + 0.0001436t - 0.000000001975t^2$.

Neglecting the last term, and changing to degrees absolute, we obtain the formula for the atomic heat used above.

In using this formula in the calculation of L_0 , however, it must be remembered that the specific heat of carbon decreases very rapidly at low temperatures, the specific heat of diamond at the interval -188° to -252° being, according to Dewar (*Proc. Roy. Soc.*, 1905, **76**, 325), as low as 0.0043. The value obtained for $L_0=38,055$ is therefore probably too high; but the relative values of L between 1073° and 1373° Abs. will not be greatly affected, and the correction should suffice to show to what extent the change in the value of L with temperature alters the value of the equilibrium constant.

Le Chatelier's formula, as applied to the system under consideration, can now be put in the form:

$$\frac{1}{2} \cdot \frac{38,055 + 2 \cdot 02 T - 0 \cdot 0031 T^2}{T} + \log_e P + \log_e \frac{C_1^2}{C_2} = k \dots (ii).$$

Whence, using the calculated values of C_1 and C_2 at atmospheric pressure given in the preceding table, we obtain:

Cemperature,		
Abs.	k.	
1073	18.76	
1123	18.75	
1173	18.74	
1223	18.74	
1273	18.74	
1323	18.74	
1373	18.75	

The apparent linear increase in the value of k when L is regarded as constant is therefore accounted for by the change in the value of L with temperature, and it is possible to apply a correction deduced from the known changes in the values of the specific heats of the reacting substances.

Whilst too great reliance cannot be placed on the value of the constant when approaching the limits of the system, it may be noted that the theoretical temperature at which the reaction $CO_2 + C \rightarrow 2CO$ should be still appreciable is, at atmospheric pressure, about 588° Abs., at which temperature about 0.10 per

cent. of carbon monoxide should be formed. Boudouard, using finely divided nickel as catalyst, claims to have obtained complete dissociation of carbon monoxide at a temperature of 718° Abs., thereby implying that the reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ is not reversible below that temperature. His observations are not confirmed, however, by Smitz and Wolff (*Zeitsch. physikal. Chem.*, 1903, **45**, 199), who, using a similar method of experiment, obtained distinct



reversal at 718° Abs. Sabatier and Senderens (*Bull. Soc. chim.*, 1903, [iii], **29**, 294) state that total dissociation of carbon monoxide occurs at a temperature lying between 503° Abs. and 673° Abs.

The effect of pressure on the equilibrium at any one temperature is strictly in accordance with Le Chatelier's formula. If pressures in atmospheres are taken as ordinates and percentages of carbon dioxide as abscissæ, the points of intersection lie on a curve which at high temperatures is practically a straight line passing through

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AND OF PRESSURE ON THE EQUILIBRIUM $2CO \equiv CO_2 + C$. 1147

In Fig. 1 the results of our experiments are shown the origin. graphically in this manner, the curves being drawn through points calculated from equation (ii), and the values found by experiment being indicated by different symbols for each temperature.

30 25 $\mathbf{20}$ Carbon dioxide : per cent. 15 10 **P** 5 900 1000 1100 1200 Temperature °C.

The curves in Fig. 2 show in a similar manner the variations in the percentages of carbon dioxide with temperature at 0.5, 1, 2, and 3 atmospheres pressure, as determined from our experiments; whilst we have added a curve for $\frac{1}{2}$ atmosphere, shown in dotted

FIG. 2.

line, calculated from equation (ii) and representing the effect of the passage of a slow current of air through excess of carbon.

EXPERIMENTAL.

The apparatus employed, which is shown diagrammatically in Fig. 3, consists essentially of a "reaction vessel" in the form of a stout-walled bulb of fused quartz (A), closed by a high pressure



tap (B) of the same material; a mercury manometer (F); and an exhausted glass globe (G), into which a sample of the gases contained in the quartz bulb can be rapidly passed.

The bulb is 11 cms. long and of 3 cms. external diameter, and has a capacity of about 52 c.c. when empty. It is one-third filled with purified wood-charcoal (prepared in the manner described in our previous paper), crushed, and sieved so as to pass through a 10-mesh sieve and remain on a 30-mesh. The weight of charcoal originally introduced into the bulb was 6 grams.

AND OF PRESSURE ON THE EQUILIBRIUM $2CO \equiv CO_2 + C$. 1149

The quartz tap, which is of fine capillary bore, is fused as close as possible to the neck of the bulb, and makes connexion by means of a ground-joint (C) with a glass capillary **T**-piece. To one limb of this **T**-piece is fused a three-way tap (E), and to the other a mercury-cup tap (D) leading to the globe. The three-way tap communicates with the manometer, the side-tube admitting of the adjustment of the head of mercury to bring the short column to a constant level when measuring the pressure inside the bulb.

The bulb is heated in an electric resistance furnace (K), the refractory tube of which is wound with fine platinum wire, the coils at the end through which the neck of the bulb passes being placed close together to compensate for loss of heat by radiation from the furnace at that end, which is purposely left unprotected by heat-insulating material. This arrangement enables a zone of uniform temperature to be obtained throughout that portion of the furnace occupied by the bulb; that is to say, over a distance of 11 cms., starting 4 cms. from the mouth of the furnace. The "dead-space" between the bulb and the quartz tap amounts to less than 0.5 c.c., or about 1 per cent. of the total volume of the reaction The tap is kept cold by a rapid stream of water, which is vessel. prevented from entering the furnace by a quartz collar (L) fused to the neck of the bulb. The mouth of the furnace-tube is closed by tightly packed asbestos fibre.

Temperatures are measured by means of a platinum and platinumrhodium thermo-couple passing along the bottom of the furnace tube, the junction being at J.

For the obtaining of a constant temperature during prolonged periods, a modification of the device described in our previous paper has been used (*loc. cit.*, p. 2185). This modification, which consists simply of the passage of the electric current through two sets of Nernst steadying resistances in series, has had the effect of ensuring a rigid maintenance of the experimental temperature during many days, and constitutes an improvement on our previous method.

Method of Conducting an Experiment:—The whole apparatus having been exhausted through the tap H, dried carbon dioxide or monoxide is introduced from a gas-holder, in which it has been stored during several days over concentrated sulphuric acid. The bulb containing the carbon is usually kept at a temperature of 200° whilst being filled, since below that temperature rapid absorption of the gas takes place. The tap B is then closed, and the remainder of the apparatus thoroughly exhausted. On now heating the furnace to the required experimental temperature, the expansion of the gas in the bulb creates a pressure which reaches from three to four atmospheres, dependent upon the temperature and pressure at

which it was filled, and on the amount of absorption that has been allowed to take place during filling.

After leaving a sufficient length of time for equilibrium to be established, the height of the mercury column required to balance the pressure in the quartz bulb is measured, tap D being closed and tap B opened to the previously exhausted T-piece. The pressure having been determined, tap B is closed, the T-piece re-exhausted, and, B having again been opened, a second pressure reading is taken. This mode of procedure has the effect of sweeping out the dead-space in the reaction vessel should the small quantity of gas contained therein have had insufficient time to diffuse; and it enables a correction to be applied for the reduction of pressure in the reaction vessel when it is first opened to the exhausted **T**-piece (the capacity of which is about 1 c.c.), the pressure-reading required being that existing in the bulb before tap B is first opened.

A sample of the gases is obtained by momentarily turning the tap D on to the exhausted globe. In this manner the sample is instantaneously cooled below the temperature at which reaction can take place, and the pressure in the reaction vessel is reduced. The whole of the sample in the globe is then withdrawn through a mercury vacuum pump and analysed.

The volume of gas allowed to escape into the globe from the reaction vessel has usually been sufficient to reduce the pressure in the latter by about half an atmosphere. Heating is then continued at this lower pressure during a sufficient length of time to re-establish equilibrium, and a second sample then taken in a similar manner. In this way from five to seven samples of gas are obtained from the reaction vessel, representing the quantities of carbon dioxide and monoxide in equilibrium over carbon at the same temperature, but at pressures varying from 3 to 0.5 atmospheres.

As an example, to render the mode of operation clear, we may quote the details of experiment No. P 20.

Equilibrium Temperature = 1000° .

The reaction vessel was filled at a temperature of 300° and at 750 mm. pressure, and the temperature then raised to 1000° .

Sample 1.—After heating during twelve hours at 1000°, P = 748 + 1700 = 2448 mm. = 3.22 atmospheres.

Analysis: $CO_2 = 2.52$ per cent.* CO = 97.48 "

* The percentages are in all cases calculated as those of the "nitrogen-free" gases. The gases usually contained from 1 to 2 per cent. of nitrogen.

AND OF PRESSURE ON THE EQUILIBRIUM $2CO = CO_2 + C$. 1151

Sample 2.—After further heating during six hours at 1000°, P = 750 + 1240 = 1990 mm. = 2.62 atmospheres.

Analysis: $CO_2 = 2.06$ per cent. CO = 97.94 ...

Sample 3.—After further heating during six hours at 1000°, P = 752 + 800 = 1552 mm. = 2.05 atmospheres.

Analysis: $CO_2 = 1.75$ per cent. CO = 98.25 ,,

Sample 4.—After further heating during twelve hours at 1000°, P = 754 + 425 = 1179 mm. = 1.56 atmospheres.

Analysis: $CO_2 = 1.36$ per cent. CO = 98.64 ...

Sample 5.—After further heating during six hours at 1000°, P = 753 - 53 = 700 mm. = 0.93 atmosphere.

Analysis: $CO_2 = 0.72$ per cent. CO = 99.28 ,

We give below all the determinations that have been made at different temperatures and pressures, arranging them for convenience in tabular form in order of decreasing pressure. The values of k are calculated from equation (ii).

A series of experiments at each temperature was preceded by several preliminary trials made to determine the length of time that should be allowed for equilibrium to be established.

Temperature 800°.

Presºure.	CO_2	CO	
Atms.	per cent.	per cent.	k.
3.05	28.40	71.60	18.78
2.57	26.45	73.55	18.74
2.10	22.85	77.15	18.78
1.75	21.75	78.25	18.68
1.23	16.12	83.88	18.75
	Mean valu	ue of <i>k</i>	18.75
	Tempera	ture 900°.	
2.90	9.05	90.92	18.69
2.30	6.92	93.08	18.77
1.66	5.47	94.53	18.71
1.17	3.70	96.30	18.79
0.62	2.12	97.80	18.78
	Mean valu	ie of k	18.75

The equilibrium $2CO \rightleftharpoons CO_2 + C$.

	Tempera	ture 950°.	
Pressure.	CO ₂	CO	
Atms.	per cent.	per cent.	k.
3.18	4.42	95.58	18.85
2.71	4.32	95.68	18 72
2.48	4.07	95.93	18.69
1.95	3.65	96 31	18.56
1.69	2.50	97.50	18.83
1.21	2.04	97 96	18.78
1.21	1.90	98.10	18.71
0.68	1.11	98.89	18.78
	Mean value	e of <i>k</i>	. 18.74
	Temperat	ure 1000°.	
3.78	3.17	96.83	18.70
3.22	2.52	97.48	18.79
3.08	2.77	97.23	18'65
2.86	2.29	97.41	18.64
2.07	2.18	97.82	18.75
2.02	2.00	97.94	18.79
2 40	2 24	97 76	18.04
2.40	1.75	08.95	10.00
2.02	1.63	98.37	18.77
2.02	1.55	98.45	18.83
1.63	1.52	98.48	18.63
1.56	1.44	98.56	18.64
1.56	1.36	98.64	18.71
1.36	1.30	98.70	18.61
1.17	0.79	99-21	18.97
1.14	1.17	98.83	18.55
0.83	0.72	99.28	18.84
0.66	0.62	99.35	18.60
	Me a n value	e of <i>k</i>	. 18.71
	Temperat	ure 1050°.	
3.06	1.17	98.83	18.89
2.99	1.42	98.28	18.67
2.68	1.25	98.75	18.69
2.24	1.06	98.94	18.80
2.09	0.92	99.08	18.76
1.09	0.47	99.Z9	18.75
1.04	0.58	99 00	19.20
0.83	0.52	99·48	18.52
	Mean value	of <i>k</i>	. 18.74
	Temperatu	are 1100°.	
3.64	0.92	89.08	18.71
2.98	0.68	99.32	18.82
2.87	0.73	99.27	18.71
2.25	0.60	99.40	18.67
1.23	0.39	99.61	18.72
1.33	0.32	99.62	18.68

Mean value of k..... 18.72

isoquinoline alkaloids. Part I. 1153

Equilibrium is reached rapidly at the higher temperatures under the conditions of these experiments, but at 800° it is only attained after heating during seventy-two to ninety-six hours. At 700° the reaction $CO_2 + C = 2CO$ is extremely slow, experiments in which the gases were maintained at atmospheric pressure, by allowing release through the side-tube of the tap E (Fig. 3) dipping under mercury, only resulting in the formation of 18 per cent. of carbon dioxide after five days' heating.

This work has been undertaken in connexion with the experiments carried out by the Mining Association of Great Britain on coal-dust explosions, and forms part of an investigation into the mode of combustion of carbon.

ALTOFTS.